Kinetics of Electric field induced oxygen ion migration in epitaxial metallic oxide films

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Abstract

In this paper we report the observation of curent induced change of resistance of thin metallic oxide films. The resistance changes at a very low current (current density $J \geq 10^3$ A/cm^2). We find that the time dependence associated with the processes (increase of resistance) show a streched exponential type dependence at lower temperature, which crosses over to a creep type behavior at $T \geq 350$ K. The time scale associated shows a drastic drop in the magnitude at $T \approx 350$ K, where a long range diffusion sets in increasing the conductivity noise. The phenomena is like a "glass-transition" in the random lattice of oxygen ions.

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In recent years metallic oxides like $LaNiO_3$, $RuSrO_3$, $La_{0.5}Ca_{0.5}SrO_3$ etc. are being used as interconnects or electrodes in the field of oxide electronics. Many of these oxides belong to the ABO_3 class of oxides which are structurally similar to high T_c superconductors. In many of these oxides oxygen/oxygen defect is a particularly mobile species and the activation energy for diffusion is often $\leq$ 1eV.[1,2] The high mobility of oxygen species can lead to two generic problems in use of these oxides as interconnects or electrodes in electronic applications. First, the conductivity noise in these oxides can be substantially large which mainly arises from long range diffusion of oxygen[1]. The second problem is that the current or field induced changes in the resistivities of the films can occur for a prolonged period. This phenomenon of current induced resistance change have been first seen in high T_c oxides and studied in films of $YBa_2Cu_3O_7$ in which oxygen is a mobile species[3]. It has been concluded that the current induced resistivity change arises due to electromigration of oxygen ions. These problems are of concern because they can seriously limit their applications and cause reliability linked problems.

In this paper we investigated the kinetics of the electric field induced resistivity changes as a function of temperature in epitaxial thin films of a typical normal metallic oxide $LaNiO_{3-\delta}$ which has a cubic ABO_3 structure. The material is metallic in stoichiometric form (δ=0) and its electrical properties have been investigated extensively[4]. Our experiment consisted of high precision resistivity measurement as well as estimation of low frequency resistance fluctuations. The investigation has led to three very important results which are of significance in determining the stability of the these oxides as interconnects or electrodes. The observations are : (1) a very small current and field can induce a long time drift in the resistivity of the film, (2) the time scales associated with the changes are strongly temperature dependent and (3) at $T \approx$ 340 K - 350 K there is a drastic reduction in the time scales associated with the process and the kinetics of the resistivity variation changes over from a stretched exponential behavior (at lower temperatures) to a creep type behavior at higher temperatures. At these temperatures the conductivity noise also shows a rapid increase.

All the experiments reported here are done with thin epitaxial films (thickness $\approx$ 150

nm) of $LaNiO_3$ grown on $LaAlO_3$ substrate by pulsed laser ablation. Details of growth and characterization has been given elsewhere.[5,6] Films with room temperature resistivity $\rho_{rt} = 1.6$ mΩ.cm were patterned for resistance and noise measurements. The resistance measurements were done with a precision of 1 ppm and the noise measurement using a five probe geometry[7] was done with precision of spectral power $\leq 10^{-19}$ V^2/Hz. All the data are taken at thermal equilibrium where the temperature was controlled to within ± 5 mK.

In figure 1 we show a typical current induced change in the observed resistance R at three characteristics temperatures. The measurements shown here were made with a current of 100 mA. This corresponds to a current density $J \approx 5\times10^4$ A/cm^2 and an electric field $E \approx 10^2$ V/cm. J was so chosen that it was not high enough to cause a rupture and at the same time not so low that no perceptible change occurs. (We find that there is a threshold associated with this phenomena with $J_{threshold} \leq 10^3$ A/cm^2 and the exact value depends on the history of the material). Immediately after applying the current the resistance (R) drops slightly in a scale of few minutes. Then it starts to increase. We call this the "damage"-(d) process. Over several hundred minutes R changes by about $\sim$ 2-3%. Then the current was reversed. On reversal of current R falls typically by $\leq 1\%$ and then starts to increase again. We call this drop in resistance the "recovery" (r) process. The time scale involved in the $r-$process is much smaller than that involved in the $d-$process and it is quite similar to the early resistance drop seen on initial application of the current. The current stressing experiments were done for 270 K $< T <$ 400 K. Similar $r-$ and $d-$processes were seen in epitaxial films of high T_c cuprates at room temperature[3]. It was concluded[3] that the resistance change is a consequence of the oxygen ion migration and while the $r-$process heals defects, the $d-$process increases the defect and disorder. In this letter however we donot discuss this issue and focus on the kinetics instead, in particular its temperature dependence.

It is also important to note that the process occurs at low current/field. The current density J used in the experiment is much less than the typical electromigration threshold observed in metallic interconnects. Interestingly this is also less than the threshold of $J \approx$

10^6 A/cm^2 observed in high T_c cuprates[3].

In order to obtain quantitative evaluation of the time scales we first fitted the data to the following functional form.

$$\Delta R(t) = \Delta R_r(t) + \Delta R_d(t) \tag{1}$$

where the subscripts refer to the $r-$process and the $d-$process. Here we assume that the two processes take place simultaneously. However they are well separated in time and thus it is possible to analyze the data unambiguously. Both ΔR_r and ΔR_d follow *streched* exponential dependence on time t. For ΔR_d an additional creep component shows up at $T = 350$ K and dominates the t dependence at higher T. Thus we can write :

$$\Delta R_r = \Delta R_{0r} \left[1 - e^{-(t/\tau_r)^{\beta_r}}\right] \tag{2}$$

at all T.

$$\Delta R_d = \Delta R_{0d} \left[1 - e^{-(t/\tau_d)^{\beta_d}}\right] + \nu t \tag{3}$$

where $\nu = 0$ for $T < 350$ K. At low temperatures ($T < 330$ K) τ_d being very large compared to the measurement time t an unambiguous and independent determination of τ_d and ΔR_{0d} is not possible. Instead, $\tau_d \gg t$ allows us to make the assumption that

$$\Delta R_d = \left(\frac{t}{K}\right)^{\beta_d} \tag{4}$$

where,

$$K = \frac{\tau_d}{(\Delta R_{0d})^{1/\beta_d}} \tag{5}$$

The data are fitted to the eqns.1-5 and the parameters are obtained. Typical time dependence of the resistance is shown figure 1. The inset to figure 1 shows a few fits to the data according to the equations above.

The time scale for the recovery process τ_r follows an Arrhenius relation with T with an activation energy $E_r = 0.79$ eV which is the same as the activation energy for migration

of oxygen ions in these materials.[1,2] This shows that the process of current induced change in R has its origin in oxygen ion migration. Also the exponent $\beta_r \approx 0.8$ implying that the underlying process is not too different from a simple Debye relaxation ($\beta = 1$).

The temperature dependence of the time scale for the d-process, τ_d is shown in figure 2. In this case we show the temperature dependence of K (see eqn 5) which in turn shows the T dependence of τ_d since the T dependence of ΔR_{0d} is less severe. We find that K (and hence τ_d) has a weak temperature dependence for $T < 340$ K. But at $T = 350$ K, K drops drastically. In the same graph we have also shown the T dependence of the creep rate ν. This is small near $T = 350$ K and increases rapidly at higher T. The creep rate also follows an Arrhenius temperature dependence with activation energy, $E_d = 0.84$ eV. This again is similar to E_r and is similar to the activation energy for oxygen ion migration. The physical process underlying the resistance change is thus related to the migration of oxygen ions.

Figure 2 clearly shows that there is onset of long range diffusion at $T \geq 350$ K which gives rise to the creep. The effect of long range diffusion for $T \geq 350$ K can be seen also in the conductivity noise (denoted by γ/n, normalized noise magnitude, n being the carrier concentration) which we show in the lower part of figure 2. One can see that at the onset of the long range diffusion the temperature dependence of the noise shows an upturn at $T \approx 350$ K. The fact that the extra noise observed at $T \geq 350$ K arises from long range diffusion has been shown before.[1] Below this temperature long range diffusion is frozen-in. The situation is thus similar to the process of glass-transition where at certain characteristic temperature range the long range diffusion freezes on cooling.

Evidence of a glass-transition like freezing at $T \approx 350$ K can be seen also in the T dependence of the streched exponential exponent β_d which is shown in figure 3. The value of the exponent β_d is high in the "molten" state ($T > 350$ K) signifying nearly single Debye type relaxation associated with the oxygen migration. However, in the frozen state ($T < 350$ K) the value of β_d sharply decreases to $\approx$ 0.4-0.6 implying that there is an hierarchy of the relaxation process as in a glass[8]. Interestingly, in a recent noise studies at low temperatures ($T < 20$ K) we found clear evidence of two-level systems of low energy in this crystalline

material as one generally find in conventional glasses[9]. In that study we were able to conclude that these "glass like" low energy excitations occur in the randomly frozen lattice of oxygen ions. The observation of kinetic freezing at $T \approx 350$ K thus very well connects to the observation of low energy excitation.

The observation of a glass like freezing of the oxygen migration is a new result. (However, there exists evidence from calorimetric studies of a glass-transition like phenomena of the excess oxygen in a related compound La_2NiO_4[10].) We feel that this new phenomena will be extremely important in determining the usability of oxide films as interconnects or electrodes. The important lesson from our investigation is that the characteristic temperature, where the "glass-transition" of oxygen ions occur should be at a fairly high temperature if these oxide interconnects have to be used in application with low noise and stability against field-induced oxygen ion migration.

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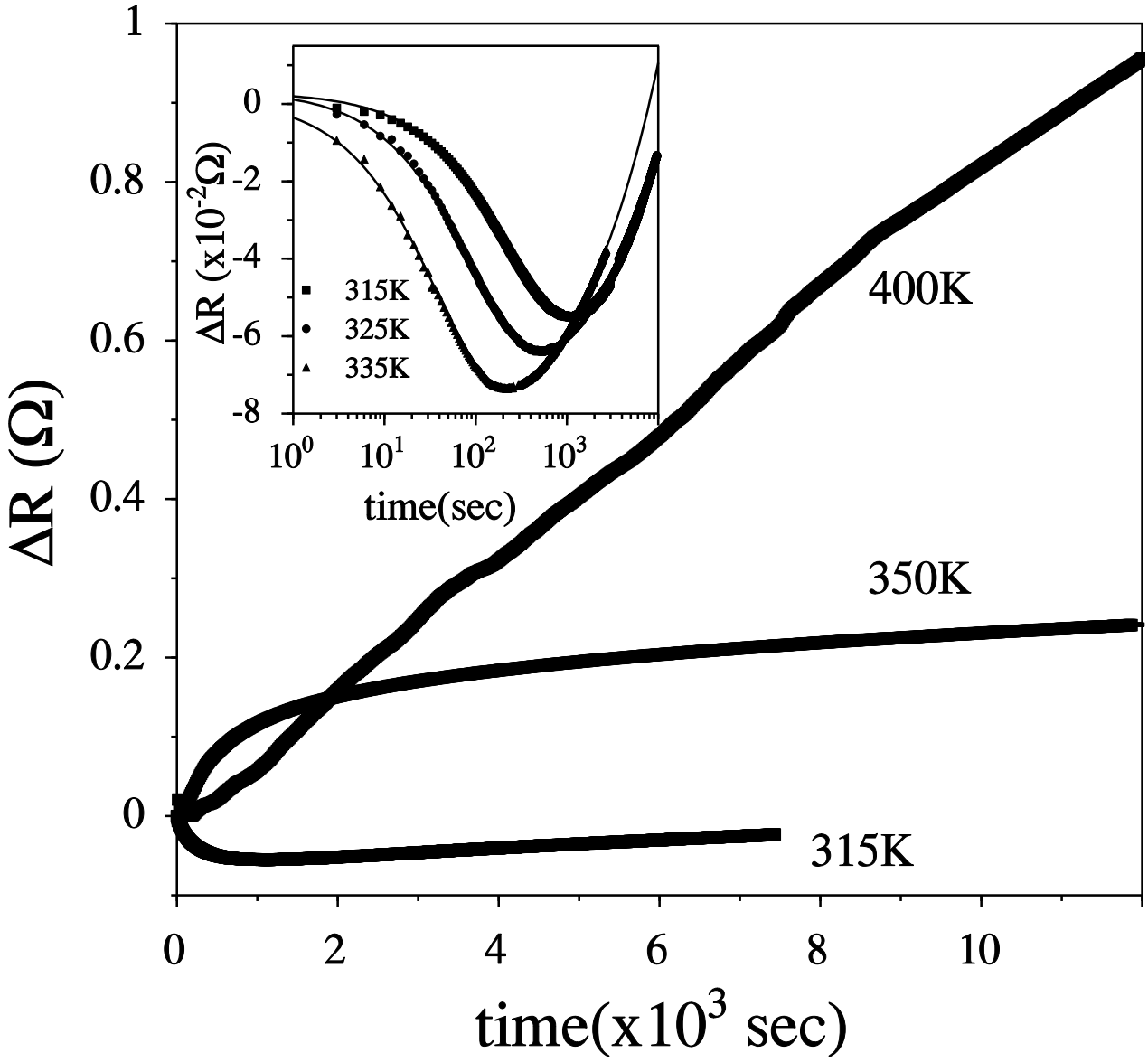
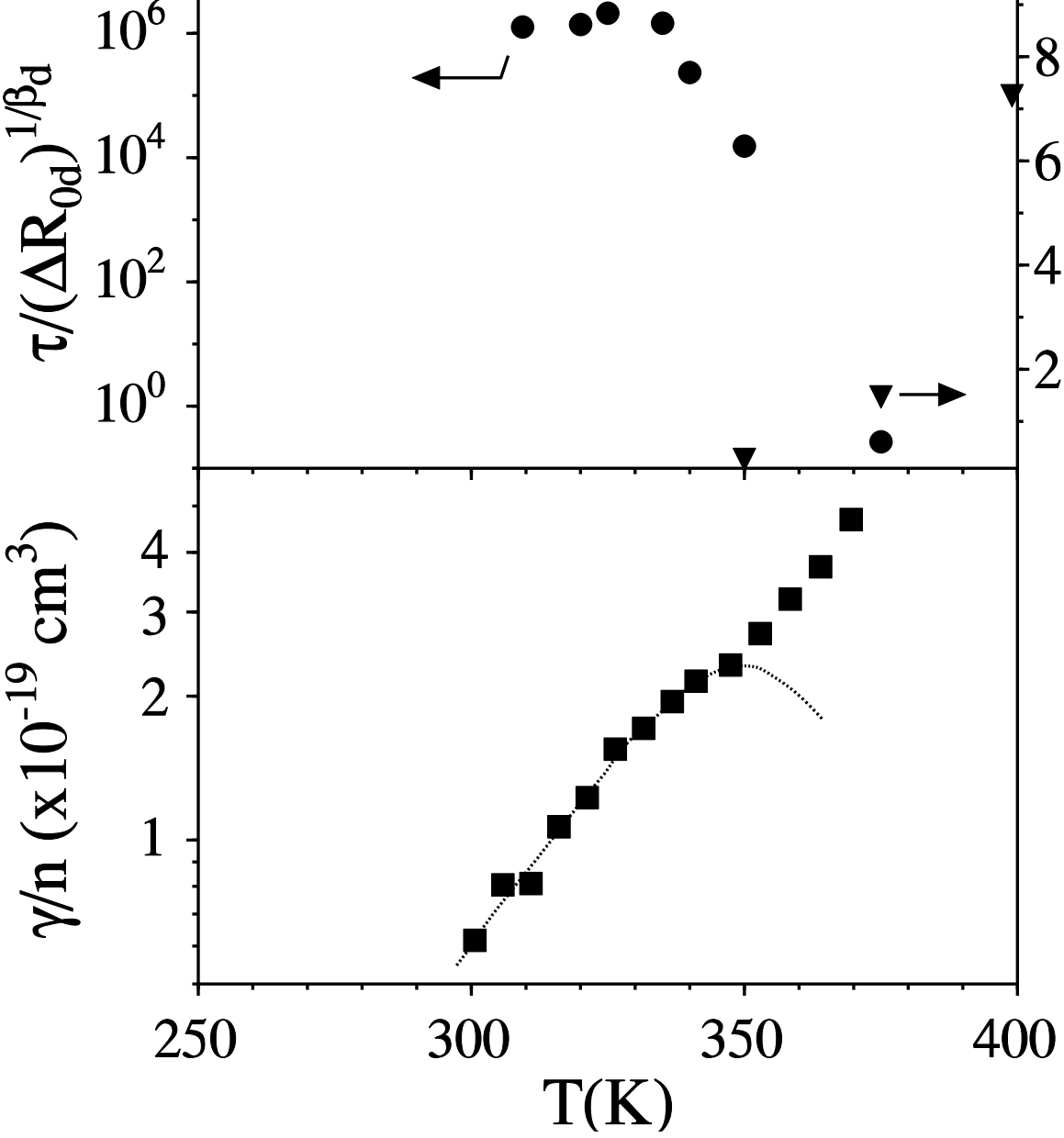
Figure Captions

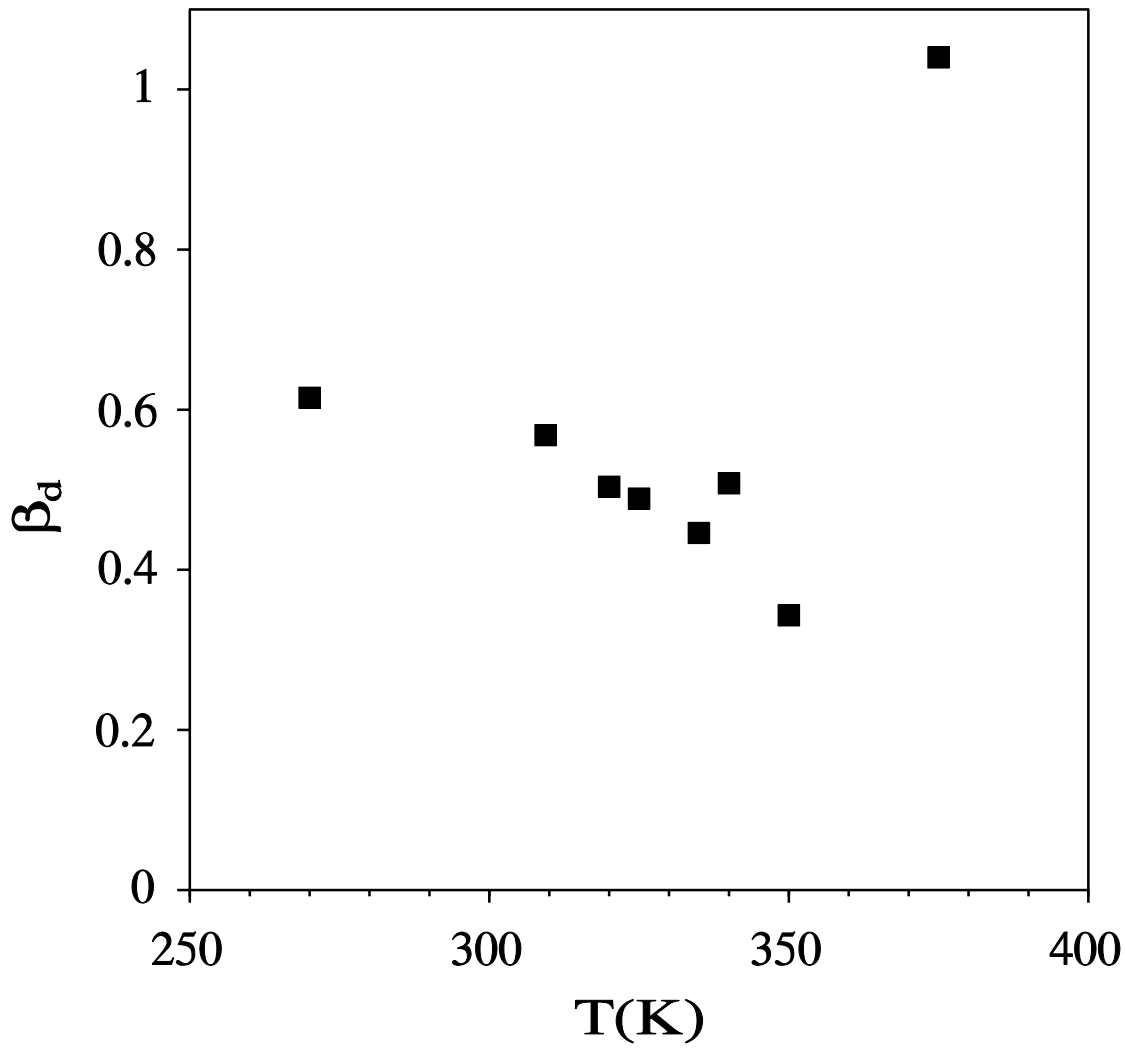
Figure 1: Time dependence of resistance at various temperatures. The data at 400 K depicts creep-type behavior and the change in resistance is irreversible. The inset shows the type of fit that can be obtained with the phenomenological equations described in the text.

Figure 2: Temperature dependence of K (see text) and normalized noise magnitude. Current density for noise measurement was $\leq 10^3$ A/cm^2. The dotted line in the noise curve is guide to the eye showing the expected temperature dependence due to localized movements of atoms/vacancies.

Figure 3: Temperature dependence of the exponent β_d in the long range diffusion regime.


ΔR (Ω)
time(x10^3 sec)
400K
350K
315K
ΔR (x10^-2Ω)
time(sec)
315K
325K
335K


$\tau/(\Delta R_{0d})^{1/\beta_d}$
10^6
10^4
10^2
10^0
$\nu(x10^{-5}\Omega/sec)$
8
6
4
2
$\gamma/n\ (x10^{-19}\ cm^3)$
4
3
2
1
250
300
350
400
T(K)


1
0.8
0.6
0.4
0.2
0
β_d
250
300
350
400
T(K)